

The role of seasonal turnover in lake alkalinity dynamics

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Abstract

Elemental cycles and alkalinity (Alk) production and consumption were studied in sediments from two ponds (Mares and Gull) in coastal New England. Intact cores were incubated in the laboratory and manipulated to simulate water-column anoxia during stratification and oxygenation during turnover. Reactions with S dominated Alk budgets in Mares Pond, whereas in Gull Pond reactions with N contributed most to Alk change. In Mares Pond, control cores held anoxically produced Alk at an average rate of 2.66 ± 0.59 (SE, $N = 3$) $\text{meq m}^{-2} \text{d}^{-1}$, mostly due to SO_4^{2-} reduction. This rate was similar to calculations from hypolimnetic monitoring in the pond during summer stratification. In cores from Mares Pond where the water column was aerated to simulate turnover, the reoxidation of S ($1.3 \text{ meq SO}_4^{2-} \text{ m}^{-2} \text{ d}^{-1}$) contributed most to consumption of Alk ($3.5 \text{ meq m}^{-2} \text{ d}^{-1}$); half of all Alk lost during the 40-d experiment was consumed in the first 4 d of turnover. In aerated cores from Gull Pond, Alk consumption ($4.2 \text{ meq m}^{-2} \text{ d}^{-1}$) was driven mostly by nitrification ($2.8 \text{ meq m}^{-2} \text{ d}^{-1}$). High rates of Alk consumption observed in oxidized cores illustrate the potential for rapid Alk loss during seasonal turnover.

Pore-water profiles of SO_4^{2-} and Alk suggest that sulfide oxidation was strongest in the top 1 cm of sediment and reached to a depth of 3–4 cm. Oxidation occurred rapidly in response to turnover, and although H_2S may have been oxidized initially, the oxidation of solid-phase species dominated after 1 or 2 d. An isotopic mass balance of S in two turnover cores showed that from 30 to 70% of the oxidized S originated as inorganic rather than organic S.

The acidification of lakes caused by deposition of sulfuric and nitric acids is a serious environmental problem in many parts of the world. Neutralization of this acidity begins with weathering reactions and cation exchange in the soil and plant uptake of NO_3^- in the lake catchment (Likens et al. 1977). In addition, acidity can be neutralized (alkalinity generated) during various processes occurring in the water column and sediments (Carignan 1985; Cook et al. 1986; Schindler et al. 1986) of the lake. As acidification depletes terrestrial buffering capacity, the relative importance of in-lake alkalinity generation may increase (Kilham 1982; Dillon et al. 1987).

The chemistry of alkalinity generation within lakes is fairly well understood (Stumm and Morgan 1981; Kelly et al. 1982), but there is nonetheless great vari-

ability among lakes in the magnitude of alkalinity generated and the relative importance of different processes such as SO_4^{2-} reduction or nitrification. Part of this variation is due to sedimentary characteristics, the role of epilimnetic vs. hypolimnetic sediments as influenced by morphology, and water residence time (Kamp-Neilsen 1974; Jones and Simon 1981; Kelly and Rudd 1984; Stoddard 1988). Part of the variation may also be due to the oxidation of reduced compounds following seasonal turnover. For example, SO_4^{2-} reduction generates permanent alkalinity only if the reduced, uncharged products are isolated from reoxidation—by burial, outflow, or volatile loss (Cook et al. 1986; Rudd et al. 1986a; Giblin et al. 1990). Reoxidation of reduced S, N, and Fe during seasonal turnover consumes alkalinity, and therefore the net rates of oxidation are critical in determining the net production of alkalinity in lakes.

Only recently have lake acidification models incorporated in-lake processes (Kelly et al. 1987; Baker and Brezonik 1988). If the models are to develop and incorporate seasonal dynamics, a better understanding of the seasonal changes in reactions and the role of turnover is needed. For example,

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Table 1. Location and limnological characteristics of Mares and Gull Ponds.

Characteristic	Mares Pond	Gull Pond
Location	41°35'20"N, 70°36'00"W	41°57'30"N, 69°70'30"W
Elevation, asl (m)	4.0	1.8
Surface area (ha)	11.3	44.1
Catchment area (ha)	42.0	
Max depth (m)	17.2	19.5
Mean depth (m)	7.1	9.6
Volume ($\times 10^4$ m ³)	80.4	423
Surface-water pH (0–1 m)	6.6–6.9	6.9–7.3
Sediment porosity:		
0 cm	0.94	
14 cm	0.83	

very few studies have examined alkalinity consumption specifically during turnover (cf. Cook 1981; Rudd et al. 1986b), and few data on oxidation rates are available. Part of the reason for this lack of data lies in the limitations of input-output budgets in providing process information, especially during dynamic periods such as seasonal turnover in the lake (Mortimer 1971). Rate calculations based on pore-water profiles also suffer from poor resolution when dynamic events such as turnover disrupt steady state. To overcome these difficulties we incubated intact sediment cores from two ponds in the laboratory to study the effects of oxidation on element cycles and on alkalinity production. Hypolimnetic chemistry was also monitored in the field during summer stratification. Laboratory rates were compared with field rates calculated from hypolimnetic ion budgets. Our purpose was to determine the rates and relative importance of various mechanisms that consume alkalinity during turnover and sediment oxygenation and produce alkalinity in sediments and overlying water during summer stratification.

Methods

Field site—Cores and water samples were taken from Mares Pond, 5 km inland on Cape Cod, Massachusetts; two additional cores were taken from Gull Pond, 1 km inland on outer Cape Cod (Table 1). Both are kettle ponds set in glacial till. They are circumneutral in pH, but currently receive rain of pH \approx 4.2–4.6. On the basis of hypolimnetic oxygen deficits, Rich (1980) classified

Gull as oligotrophic and Mares as mesotrophic.

Pore-water and lake-water chemistry were measured only in Mares Pond. Profiles of water temperature and chemistry were taken six times from 29 June 1988 to 16 January 1989. Water temperature was measured with a YSI model 46 telethermometer and thermistor probe. Oxygen concentrations in the ponds and sediment microcosms were measured with an Orbisphere 2714 meter and stirring probe. Light attenuation was measured with a LiCor 185 quantum meter and 2- π cosine collector. Diffuse attenuation coefficients (k , m⁻¹) were taken as the slope estimates of the regression z on $\ln(H_z)$, where H_z is downwelling PAR irradiance at depth z .

Sediment cores—Cores were taken by SCUBA divers from the deepest part of Mares Pond (17 m) on 15 September 1988. Bottom water was anoxic and had a temperature of 7.8°C. Three piston cores (6.5-cm diam) were taken to a depth of \sim 50 cm and analyzed for initial conditions. Six larger cores (microcosms; 15.5-cm diam, 50 cm tall) were taken to a depth of \sim 20 cm. The remaining core tube was filled with \sim 5 liters of anoxic bottom water. These intact cores were capped to maintain anoxia and returned to the surface. Visual inspection showed no leakage or sediment resuspension during transport. Edge effects are expected to be minor in the large-diameter cores. In addition, two sediment microcosms were taken from 15-m depth in Gull Pond on 12 September 1988. Bottom water

was anoxic in Gull Pond as well and had a temperature of 8.3°C.

All six Mares Pond microcosms were transferred to a dark, 10°C cold room and kept anoxic for 3 d. During this time SO_4^{2-} and O_2 concentrations in overlying waters were monitored and found to be similar in all cores. The overlying water in all cores was mixed continuously with magnetic stirrers. On the third day the caps of three cores (turnover cores) were removed, and the water column was stirred continuously to simulate turnover. Oxygenation of the water column above the sediment was gradual ($\sim 2.3 \text{ mg O}_2 \text{ liter}^{-1} \text{ d}^{-1}$), and after 4 d O_2 concentrations in the turnover cores were similar to concentrations in the surface water. The turnover cores remained open to the atmosphere, and oxygen concentrations were close to saturation for the duration of the experiment. The remaining three cores were kept closed and anoxic during the entire experiment.

The Gull Pond cores were sandy at depth and slowly leaked overlying water during their transfer to the 10°C cold room. This leakage introduced some air, and oxygen concentrations in overlying waters the morning following collection were 1.3 and 2.9 mg liter^{-1} in the two cores. These cores were sampled for water chemistry and then opened fully to the atmosphere and bubbled with air to simulate turnover. The bubbling continued during the entire experiment and also served to mix the overlying water. Because oxygen introduction may have stimulated oxidation before the first sampling, we made no initial rate estimates.

Sediment handling and analyses—Mares Pond cores were sectioned in a glove bag filled with N_2 . One initial, one final turnover, and one final anoxic core were sectioned at 1-cm intervals to 14-cm depth. The two remaining cores from each treatment were sectioned from 0 to 6 cm at 1-cm intervals and then at 2-cm intervals down to 14 cm. Each sediment section was homogenized, and subsamples were transferred to glass jars in the glove bag and then frozen at -20°C . Pore water was extracted from a subsample of fresh mud by centrifugation and kept under N_2 until analysis. Porosity was determined on two cores by

weighing known volumes of wet mud and drying at 105°C . The averaged porosity values were used for all further calculations. Total sulfur (S_T) was measured on similarly dried samples with a LECO SC-32 sulfur analyzer and commercial standards. Sample replicates deviated on average by $1.9 \pm 0.5\%$ (± 1 SE of the mean; $N = 9$). Oven- and freeze-drying of lake sediments can result in the loss of S and changes in S isotopic ratios (Amaral et al. 1989). We do not know if such losses were important in our study, but we expect that only our results for organic S would be affected by drying. S_T was corrected for pore-water contributions of SO_4^{2-} and sulfide and reported per gram dry weight of sediment. Freeze-dried samples were analyzed for reduced inorganic S by heating in an acid Cr(II)Cl_2 solution (Howarth and Merkel 1984). Liberated sulfide was trapped in a Zn acetate solution and then measured colorimetrically. This Cr-reducible S (CRS) includes Fe monosulfides, FeS_2 , and elemental S.

Water sampling and analyses—Lake-water chemistry was monitored during summer stratification and into the winter following turnover. Overlying water in the microcosms was monitored for 39 (Mares) or 47 d (Gull) after introduction of oxygen (turnover). Pore-water profiles for most ions were measured on initial cores and at the end of the experiment on anoxic and turnover cores.

Overlying water from the sediment microcosms was sampled by syringe. In the anoxic cores this water was replaced with anoxic hypolimnetic pond water collected in September and again in October and stored in gastight glass bottles. Over the course of the experiment only 10% of the overlying water was replaced, and, because replacement water was chemically similar to overlying, water corrections for dilution were unnecessary.

The chemistry of pond, overlying, and pore water was analyzed similarly. Pond-water samples were pumped from depth and filtered through in-line $0.45\text{-}\mu\text{m}$ membrane filters to prevent oxygenation. Overlying water from microcosms and pore waters was filtered anoxically and analyzed or preserved immediately. Alkalinity (Alk) was

determined by potentiometric titration with H_2SO_4 . The titration curves were analyzed to determine endpoints by the method of Gran as illustrated by Stumm and Morgan (1981). In some pond-water samples Alk was determined by titration to fixed endpoints (pH = 4.5 and 4.2; EPA method); analyses agreed well. Water for SO_4^{2-} analysis was bubbled immediately with hydrated N_2 to remove H_2S species ($\Sigma\text{H}_2\text{S}$). SO_4^{2-} and Cl were then analyzed by ion chromatography (Dionex 2010i). Water for cation analyses was acidified immediately to pH 2 with HCl. Ca^{2+} , Mg^{2+} , and Mn^{2+} were determined by flame atomic absorption and Na^+ and K^+ by flame emission. Soluble reactive phosphate (SRP), $\text{NO}_2^- + \text{NO}_3^-$, and NH_4^+ were determined on a Technicon AutoAnalyzer. Dissolved Fe(II) was determined colorimetrically (Stookey 1970).

Total and reduced S isotopic compositions of sediments were determined after conversion to SO_4^{2-} and precipitation as BaSO_4 (White et al. 1989). SO_4^{2-} in pond and overlying waters was also precipitated as the barium salt. Samples were decomposed to SO_2 , purified by cryogenic distillation, and measured with a Finnigan MAT 251 isotope-ratio mass spectrometer. Results are reported relative to Canyon Diablo Troilite as a standard and calculated as

$$\delta^{34}\text{S}(\text{‰}) = [(R_{\text{sample}}/R_{\text{std}}) - 1] \times 10^3$$

where R is ($^{34}\text{S}/^{32}\text{S}$). Duplicate samples varied by $<0.2\text{‰}$.

We incubated anoxic pond water in BOD bottles in the lab as experimental controls to assess the importance of reactions in the overlying water. In two separate experiments, concentrations of NO_3^- , NH_4^+ , SRP, and SO_4^{2-} measured every 3 d showed no change over 12 and 24 d, indicating that observed changes in overlying water chemistry were due mainly to reactions in the sediments. We used the stoichiometries for these reactions as presented by Stumm and Morgan (1981) and assumed that Alk is produced on a 1 : 1 equivalent basis during reduction of SO_4^{2-} , NO_3^- , Fe^{2+} , and Mn^{2+} and that Alk is consumed on a 1 : 1 basis during oxidation of Fe^{2+} , Mn^{2+} , and sulfide. Nitrification was assumed to consume Alk on a 2 : 1 basis, one equivalent during oxidation

of NH_4^+ to NH_2OH and a second equivalent during oxidation of NH_2OH to NO_2^- or NO_3^- (Fenchel and Blackburn 1979). Cation exchange for H^+ in sediments was assumed to be 1 : 1 (equivalent).

Results

Turnover cores—Initial turnover in Gull Pond resulted in the appearance of SO_4^{2-} and the consumption of Alk in overlying waters (Fig. 1). After day 7, however, SO_4^{2-} reduction in the sediments removed SO_4^{2-} from the overlying water and generated Alk. SO_4^{2-} reduction continued at a roughly constant rate until day 16, but from then on reduced S oxidation and net release of SO_4^{2-} to overlying waters again dominated S dynamics in both cores. This switch from production to consumption of Alk was mediated by nitrification as well as sulfide oxidation, reactions that take place in oxic zones close to the sediment surface and thus are sensitive to small changes in depth of oxygen penetration.

The period of SO_4^{2-} reduction is interpreted as an equilibration of sediment microbes to oxygenation of surficial sediment. A new zone of SO_4^{2-} reduction must have developed at a lower sediment depth, perhaps stimulated by increased SO_4^{2-} availability from above and perhaps by the availability of newly degraded organic matter produced by aerobic bacteria. SO_4^{2-} reduction rates during this time were slower than rates found during anoxic stratification in Gull Pond ($0.4 \text{ mmol m}^{-2} \text{ d}^{-1}$; unpubl.) or in anoxic Mares Pond mud (Table 2) and were similar to calculated rates in epilimnetic sediments (Kelly and Rudd 1984; Rudd et al. 1986b; Schiff and Anderson 1987). Thus the Gull Pond cores behaved similarly to some other sediments exposed to oxygenated water where SO_4^{2-} reduction at depth can exceed sulfide oxidation at the surface.

Nitrification was delayed following turnover and occurred at a much greater rate in one core. Beginning on day 30 in core G1, NH_4^+ concentrations fell ($2.13 \text{ mmol m}^{-2} \text{ d}^{-1}$) and NO_3^- concentrations rose ($1.42 \text{ mmol m}^{-2} \text{ d}^{-1}$) until the end of the experiment (Table 2; Fig. 1). In core G2, however, nitrification was much less important and

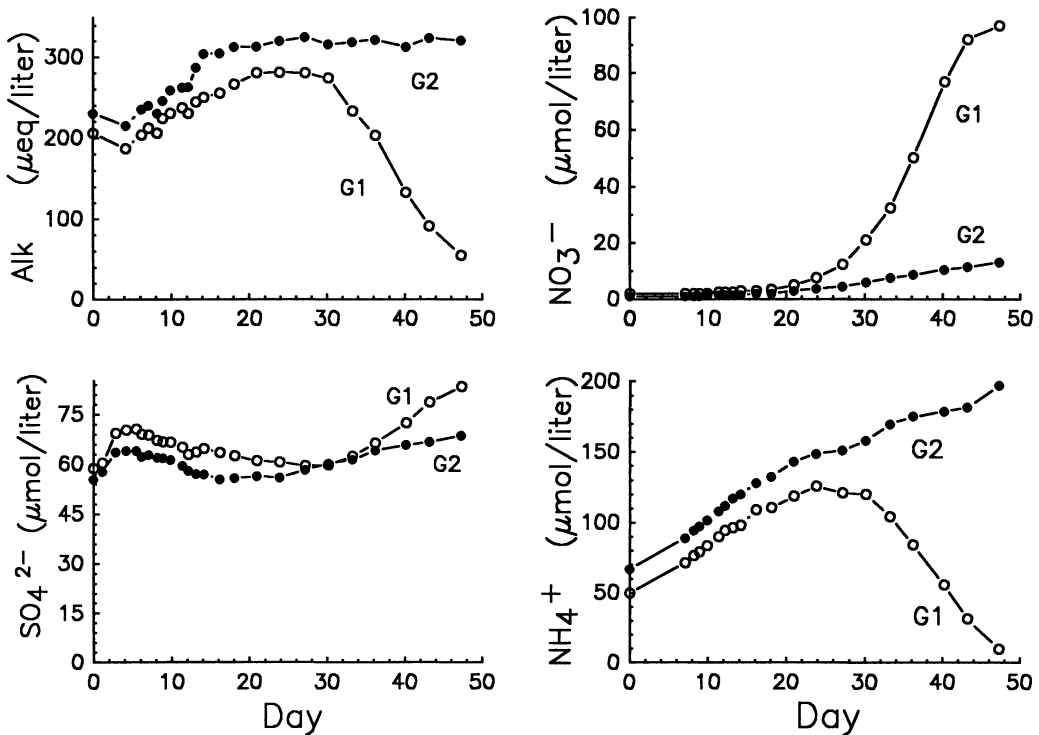


Fig. 1. Time-course of changes in Alk, SO_4^{2-} , NO_3^- , and NH_4^+ in overlying water in two sediment microcosms (G1 and G2) from Gull Pond.

NH_4^+ concentrations increased in overlying waters for the whole experiment. The reason for this variability between cores is unclear, although conditions optimal for nitrification appear to be very sensitive to small changes in sedimentary characteristics or to the penetration of oxygen into surface layers (Chen et al. 1972). Jones and Simon (1981) found that the potential for nitrification was much greater in epilimnetic (higher E_h) vs. hypolimnetic sediments of Blelham Tarn. The degree of initial drainage due to leaking before turnover also may have affected nitrification rates differently between cores.

In the turnover cores from Mares Pond, SO_4^{2-} and NO_3^- appeared in the overlying water, while Alk, NH_4^+ , and Fe^{2+} were consumed (Fig. 2). The rate of Alk consumption was highest and relatively constant from day 3 to 10 ($-3.50 \text{ meq m}^{-2} \text{ d}^{-1}$) and then declined (Table 2). This initial rapid rate was due to oxidation of reduced substances such as Fe^{2+} , NH_4^+ , and H_2S in the overlying water and sediments. As these reduced

compounds were depleted from the overlying water the rate of Alk consumption slowed (Fig. 2).

Alk consumption in surficial sediments lowered pore-water Alk concentrations relative to initial profiles (Fig. 3). In addition, Alk production below the oxidized zone was unable to increase Alk concentrations at depth above concentrations found in initial cores. There is evidence for SO_4^{2-} reduction because of SO_4^{2-} depletion below 4 cm, but upward diffusion of Alk or downward diffusion of H^+ apparently produced by oxidation of sulfide, Fe^{2+} , or NH_4^+ offset Alk accumulation at depth.

Maximal rates of S oxidation occurred just after initial turnover. Sulfide oxidation was calculated as the appearance of SO_4^{2-} in overlying water. The mean oxidation rate over the first 7 d was $0.67 \text{ mmol m}^{-2} \text{ d}^{-1}$, which was equal to the rate of SO_4^{2-} reduction in the anoxic cores. H_2S may have been the primary compound oxidized in the first 2 d following turnover. The mean inventory of H_2S in the overlying water of microcosms

Table 2. Ionic fluxes (± 1 SE) in microcosm sediment cores from Mares and Gull Ponds, and in the hypolimnion of Mares Pond 6–30 September. The 6–30 September interval corresponds most closely to the time when sediment microcosms were collected (15 September). The periods over which mean flux rates were calculated are given in parentheses; e.g. fluxes were calculated for Gull Pond during days 7–16 and 30–47 (see Figs. 1, 2).

	Ion flux ($\text{mmol m}^{-2} \text{d}^{-1}$)					
	Alk ($\text{meq m}^{-2} \text{d}^{-1}$)	SO_4^{2-}	NH_4^+	NO_3^-	Fe^{2+}	SRP
Mares						
6–30 Sep	2.28	-0.68	0.40	—	0.47	0.016
Mares anoxic cores						
(day 3–22) $N = 3$	2.66 ± 0.59	-0.66 ± 0.11	0.46 ± 0.10	—	0.44 ± 0.13	0.08 ± 0.018
(day 3–42) $N = 3$	1.56 ± 0.30	—	0.45 ± 0.06	—	0.09 ± 0.04	0.06 ± 0.008
Mares turnover cores						
(day 3–10) $N = 3$	-3.50 ± 0.36	0.67 ± 0.16	-0.32 ± 0.05	0.29 ± 0.01	-0.37 ± 0.10	—
(day 3–42) $N = 3$	-1.02 ± 0.06	0.18 ± 0.03	-0.15 ± 0.01	0.20 ± 0.02	-0.10 ± 0.02	—
Gull (day 7–16)						
Core G1	1.59	-0.29	1.28	0.03	—	—
Core G2	1.56	-0.30	1.01	0.03	—	—
Gull (day 30–47)						
Core G1	-4.24	0.42	-2.13	1.42	—	—
Core G2	0.06	0.10	0.50	0.10	—	—

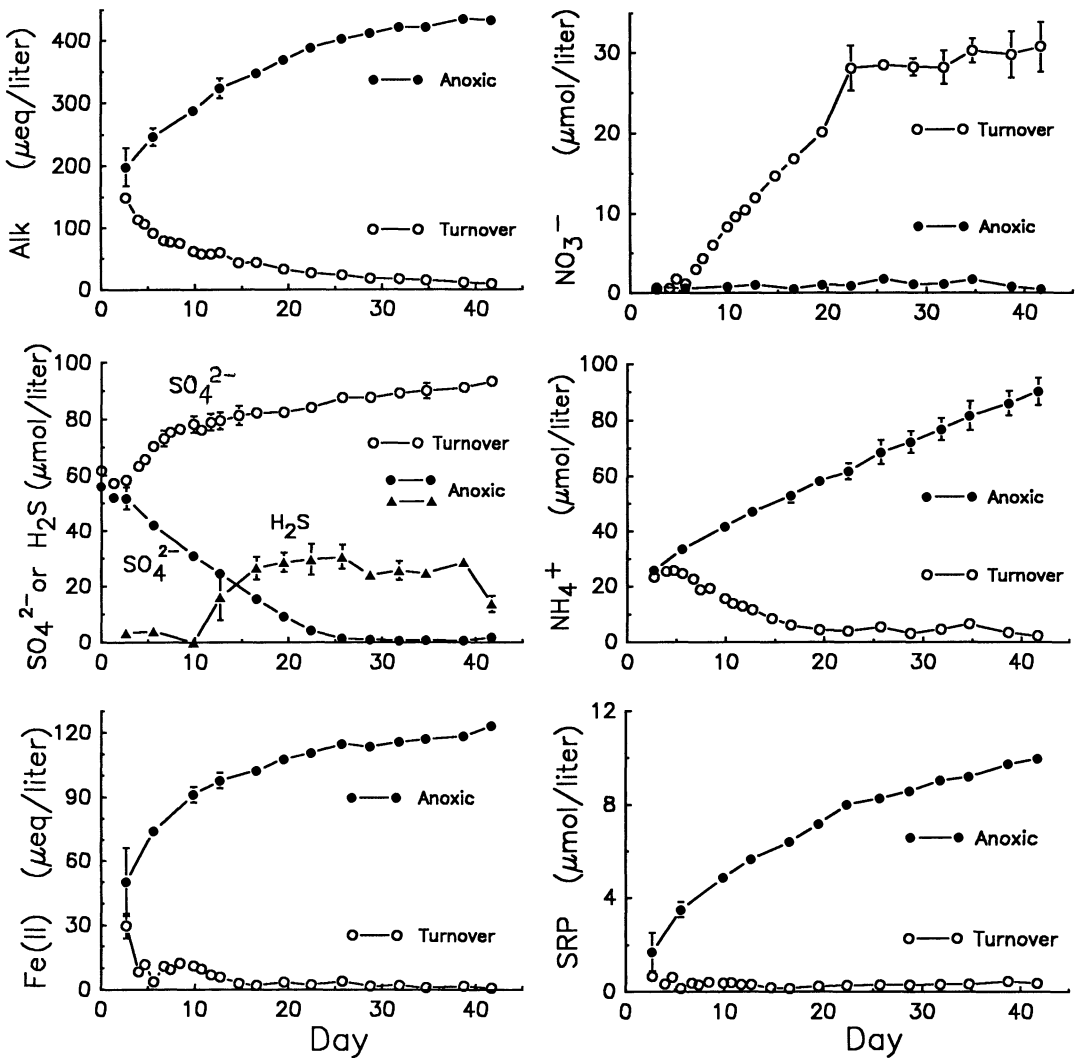


Fig. 2. Time-course of changes in chemistry of overlying water in sediment microcosms from Mares Pond. Each data point is a mean of three replicate cores; error bars represent ± 1 SE. Lack of error bars means that variability is smaller than symbol size. SO_4^{2-} measurements begin at day 0; all other ions were measured starting on day 3.

before turnover was 0.89 ± 0.14 (SE) mmol m^{-2} , and the initial inventory of H_2S in the upper 3 cm of pore water was 0.35 mmol m^{-2} . Together this amount of H_2S could supply the observed amount of oxidation for up to 2 d. After 1 week the rate of SO_4^{2-} release from the sediments slowed substantially. As discussed below, these different rates may represent a change in the form of reduced S oxidized (H_2S , FeS , FeS_2 , and organic S).

SO_4^{2-} concentrations in the pore water of turnover cores were controlled by the balance between SO_4^{2-} reduction at depth and oxidation at the sediment surface (Fig. 3). Net depletion of SO_4^{2-} occurred below 4 cm in all cores. Above 4 cm, higher SO_4^{2-} concentrations in turnover relative to initial cores indicated significant oxidation of reduced S. Because a positive flux of SO_4^{2-} from the sediments continued throughout the turnover experiment, there must have

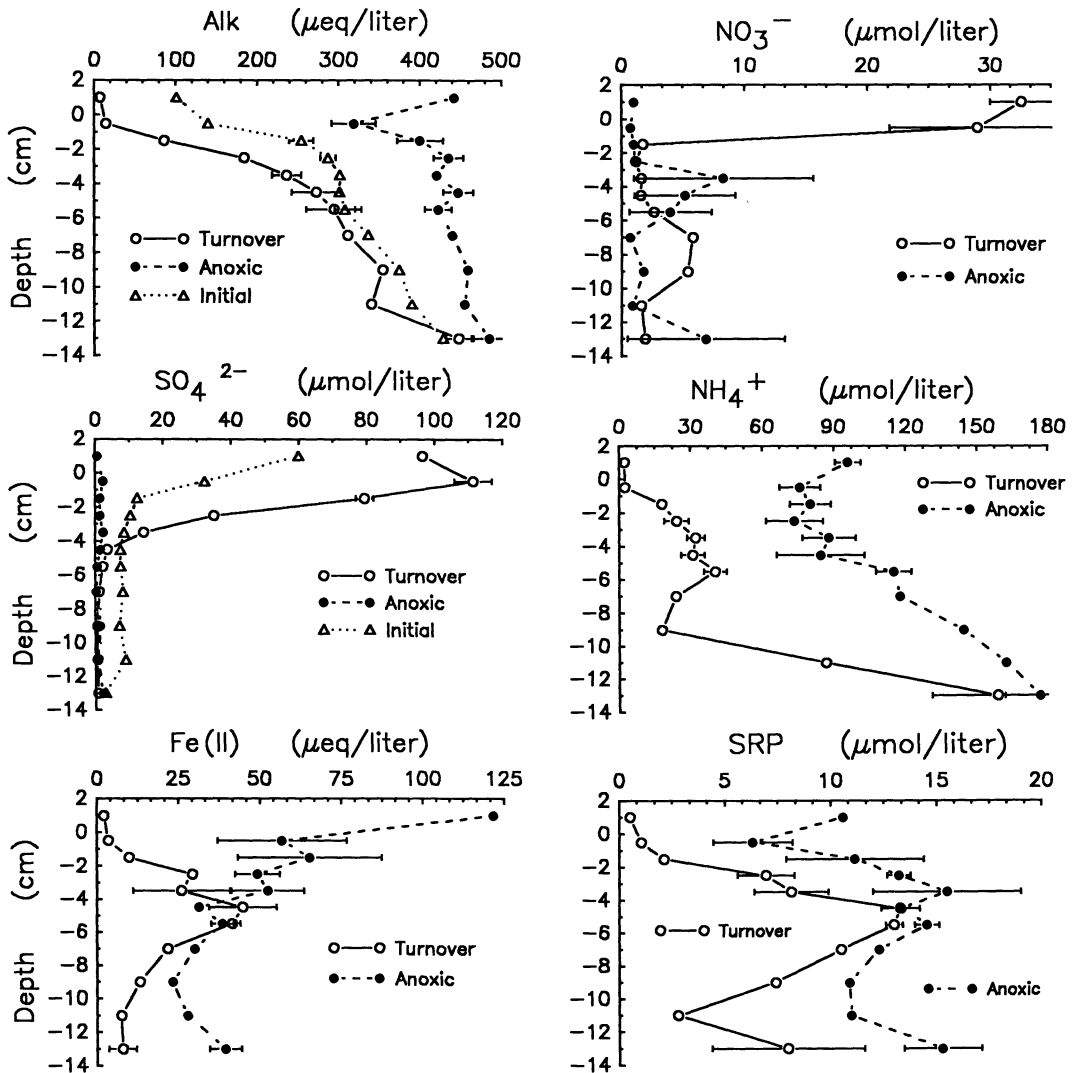


Fig. 3. Pore-water profiles for chemical species in sediment microcosms from Mares Pond. Initial profiles (SO_4^{2-} and Alk only) are compared to profiles measured in turnover and anoxic microcosms at the end of a 40-d experiment. Each data point is a mean of three (for anoxic and initial) or two replicate cores (for turnover) from 0 to -6 cm and at -14 cm (error bars represent ± 1 SE). Values between -6 and -14 cm were determined from one core. Mean values ($N = 3$) for overlying waters are plotted at $+1$ cm.

been a steep, negative pore-water SO_4^{2-} gradient between 0 and 1 cm that was obscured by the 1-cm sampling intervals. This influence implies that S oxidation was most rapid in the top 1 cm of sediment. Overall, S oxidation accounted for 38% of the total Alk consumed in the first 7 d after turnover began.

NO_3^- increased linearly for the first 20 d

after simulated turnover began, but after this time concentrations remained relatively constant (Fig. 2). Nitrification is probably the process responsible for these changes; the mass of NH_4^+ lost is fully balanced by NO_3^- appearance, and NO_3^- buildup ceased after complete consumption of NH_4^+ from overlying waters (Fig. 2). Concentrations of NO_3^- around $30 \mu\text{M}$ in overlying waters

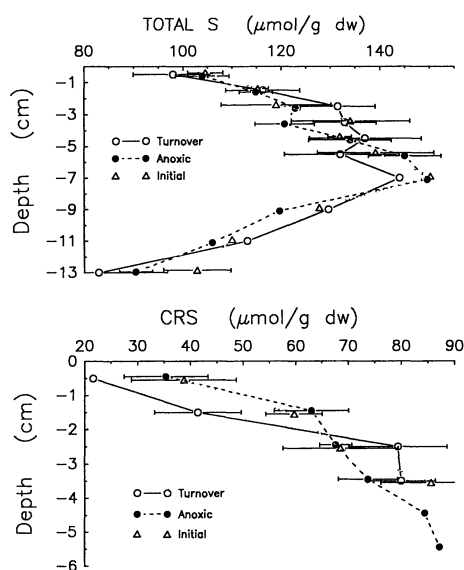


Fig. 4. Total S and CRS in cores and sediment microcosms from Mares Pond. Mean initial values ($N = 3$) are compared to turnover ($N = 2$) and anoxic ($N = 3$) values at the end of a 40-d experiment (error bars represent ± 1 SE).

were reduced to $< 2 \mu\text{M}$ in pore water by the 2-cm depth (Fig. 3). Similar sharp NO_3^- decreases in surficial sediments are commonly observed (Rudd et al. 1986b) and are due to denitrification.

Rates of nitrification were almost 5 times lower in Mares than in Gull sediments (Table 2). Nitrification rates were not a simple function of NH_4^+ concentration; even though ambient levels of NH_4^+ were twice as high in Gull Pond as in Mares, nitrification rates were higher in only one of the two Gull Pond cores compared to rates in Mares Pond (cf. Andersen 1977). Nitrification rates similar to those in Mares and Gull Ponds have been observed elsewhere ($\sim 1 \text{ mmol N m}^{-2} \text{ d}^{-1}$, Mortimer 1971; $0.9\text{--}1.7 \text{ mmol N m}^{-2} \text{ d}^{-1}$, Jones and Simon 1981; $\sim 0.2 \text{ mmol N m}^{-2} \text{ d}^{-1}$, Chen et al. 1972).

Cation fluxes (other than Fe and NH_4^+) in the overlying waters of all cores from both Mares and Gull Ponds were small in magnitude and random in sign during the experiment. None of the regressions of cation concentrations vs. time had a slope significantly different from zero ($P > 0.1$). Although Alk contributions from exchange of major cations with H^+ in the sediments were

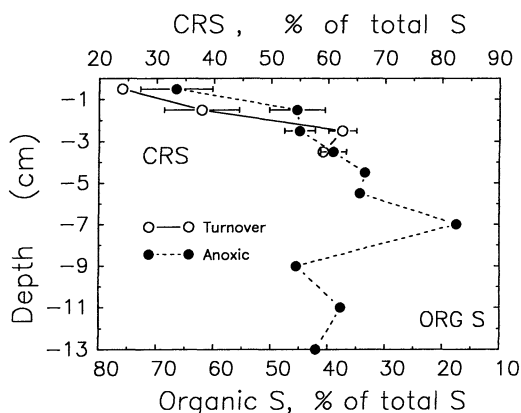


Fig. 5. Fraction of CRS and organic S as a percentage of total S in turnover and anoxic treatment sediment microcosms from Mares Pond.

negligible in Mares and Gull Ponds, such contributions are not trivial in some lakes (Schindler et al. 1986) and can be substantial in acid lakes (Schiff and Anderson 1986). Changes in Cl^- concentrations over time were random and below the level of precision of the analysis ($< 5\%$).

Solid-phase S—Total S concentrations in all Mares Pond cores increased from a range of $90\text{--}114 \mu\text{mol (g dw)}^{-1}$ at the surface to a range of $144\text{--}150 \mu\text{mol (g dw)}^{-1}$ at 7 cm (Fig. 4). Below this depth, S concentrations declined linearly until, at 13 cm, values ranged from 55 to $113 \mu\text{mol (g dw)}^{-1}$. Concentrations of CRS increased steadily from a range of $21\text{--}57 \mu\text{mol (g dw)}^{-1}$ at the surface to a maximum of $85 \mu\text{mol (g dw)}^{-1}$ at 6-cm depth in one anoxic core (Fig. 4). Organic S (S_{org}) was computed as the difference between S_{T} and CRS. The highest concentrations of S_{org} were at the surface, where S_{org} composed 56–78% of S_{T} (Fig. 5). Concentrations of S_{org} decreased very rapidly with depth and below 2 cm CRS dominated the S pool (49–83%). Inorganic S is a major constituent of the S_{T} pool in recent sediments in many lakes (White et al. 1989; Giblin et al. 1990), although C-bonded and ester S constitute most of the sediment S pool in others (Nriagu and Soon 1985; Rudd et al. 1986a).

Changes in solid-phase S between the anoxic and turnover treatments were not statistically significant, mainly due to among-core variability. There was, however, an indication that, from 0 to 2 cm, CRS concen-

Table 3. Mass balance of S species in two turnover cores from Mares Pond. Measured values include $\delta^{34}\text{S}$ of S_T (δS_T), of CRS (δCRS), and of initial (δI) and final (δF) SO_4^{2-} in overlying water. Calculated values include $\delta^{34}\text{S}$ of S_org ($\delta\text{S}_\text{org}$) and of the expected isotopic value of S oxidized from sediments and added to the SO_4^{2-} pool in overlying water during the experiment ($\delta\text{Oxid}_\text{sed}$). Percent $_\text{CRS}$ is the fraction of oxidized S originating from CRS, expressed as percent; S_T , CRS, and S_org indicate sediment concentrations of these S components; I and F are initial and final concentrations of SO_4^{2-} in the water column (Figs. 3, 4). All isotopic values of sediments are reported as concentration-weighted means over the depths indicated.

Turnover core	$\delta^{34}\text{S}$ (‰)						
	δS_T	δCRS	$\delta\text{S}_\text{org}^*$	δI	δF	$\delta\text{Oxid}_\text{sed}^\dagger$	Percent $_\text{CRS}^\ddagger$
3, 0–2 cm	3.7	–3.6	7.9	9.5	6.9	–0.4	70
5, 0–3 cm	4.3	–3.2	10.4	9.5	8.5	6.7	30

$$^* \delta\text{S}_\text{org} = [(\delta\text{S}_\text{T} \times \text{S}_\text{T}) - (\delta\text{CRS} \times \text{CRS})] / (\text{S}_\text{T} - \text{CRS}).$$

$$^\dagger \delta\text{Oxid}_\text{sed} = [(I \times \delta I) - (F \times \delta F)] / (F - I).$$

$$^\ddagger \text{Percent}_\text{CRS} = [(\delta\text{Oxid}_\text{sed} - \delta\text{S}_\text{org}) / (\delta\text{CRS} - \delta\text{S}_\text{org})] \times 100.$$

trations at the end of the experiment were lower in turnover cores than in anoxic cores (Fig. 4). There was also a trend of less CRS as a fraction of S_T in the turnover cores, which is consistent with oxidation of the CRS fraction during turnover.

We determined the relative amounts of CRS vs. S_org oxidized in two turnover cores by constructing an isotopic mass balance with measured $\delta^{34}\text{S}$ values for SO_4^{2-} , CRS, and S_T . Initially the $\delta^{34}\text{S}$ value of SO_4^{2-} in overlying waters was 9.6‰. At the end of the experiment $\delta^{34}\text{SO}_4$ values were 6.9 and 8.5‰, respectively, in the two cores examined (Table 3). The average isotopic value of all S released from the sediments (X_sed) was calculated by difference between the mass of SO_4^{2-} in overlying water at the beginning and the end (see Table 3). Isotopic values for S_org were calculated by difference, knowing the fraction of CRS in S_T (Fig. 5). On this basis, CRS in the two cores constituted 30 and 70%, respectively, of the S oxidized and released to the overlying water from the top 3 cm of sediment (Table 3). Small fractionation effects resulting in isotopically lighter SO_4^{2-} have been reported during oxidation of inorganic sulfide (Toran and Harris 1989), but in general these effects are negligible for both organic and inorganic S (Toran and Harris 1989). If normal fractionation effects occurred during inorganic sulfide oxidation, our estimate of percent CRS oxidized would be an upper bound.

Anoxic cores—In the anoxic cores of Mares Pond the patterns of chemical change in overlying waters were very different from changes in turnover cores. There was a net flux of Alk, Fe^{2+} , NH_4^+ , and SRP from the

sediment to the overlying water (Fig. 2). Pore-water concentrations of Alk were substantially higher in the anoxic cores compared to initial pore-water profiles (Fig. 3). Profiles in the anoxic cores were nearly vertical, and Alk accumulation in the sediment relative to initial Alk extended to nearly 12 cm. In addition, pore-water concentrations of Fe^{2+} , NH_4^+ , and SRP were higher in the anoxic cores compared to the turnover cores. The higher pore-water values coupled with accumulation of these ions in overlying waters imply production within sediments.

SO_4^{2-} was the only ion lost from overlying waters (excluding H^+), and its concentration decreased from $\sim 60 \mu\text{M}$ to $< 2 \mu\text{M}$ in ~ 25 d. We assume, because of the appearance of H_2S in the overlying water, that this loss was due to dissimilatory SO_4^{2-} reduction. H_2S precipitation with Fe could explain why the molar ratio of H_2S gain to SO_4^{2-} loss was < 1 . H_2S levels stabilized at $30 \mu\text{M}$ after ~ 15 d when SO_4^{2-} was removed completely from the overlying water. Equilibrium calculations with stability constants from Davison (1980) indicate that saturation with respect to FeS was reached in the water column at this time, and thus precipitation of FeS probably controlled Fe^{2+} and H_2S concentrations in overlying waters for the remainder of the experiment. SRP increases in the overlying water accompanied Fe^{2+} increases and most likely resulted from release of SRP adsorbed on ferric hydroxides.

The fluxes of most ions were highest initially (day 3–22) and declined as the incubation continued (Table 2). NH_4^+ release was the exception: concentrations increased linearly in the overlying water for the du-

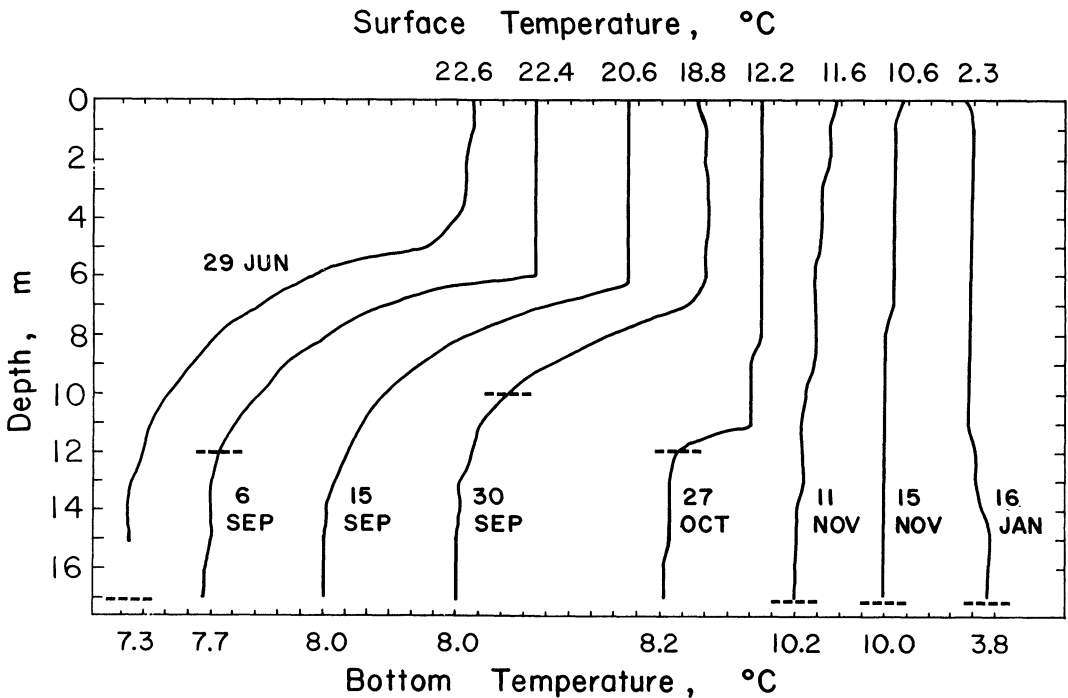


Fig. 6. History of thermal structure and depth to anoxia (<0.06 ppm O_2 ; horizontal dashed lines) in Mares Pond for June–November 1988 and January 1989. Each tick mark on the abscissa represents $1.0^\circ C$.

ration of the experiment. We believe that the main reason for the otherwise declining rates is loss of SO_4^{2-} from the overlying water and precipitation of FeS as discussed above. An additional reason for lower fluxes over longer incubation periods may be that the sedimentation of labile C was cut off in the microcosms. We have found that respiration rates of microcosms held in the laboratory for several months decrease slowly even when electron acceptors such as SO_4^{2-} are replaced continually (unpubl.). Although C input during the experiment would be small relative to the inventory of C in sediments, the quality of new inputs would be higher, and the rates of reactions occurring at the sediment surface would be considered lower bounds if C limitation occurred.

Pond water—Mares Pond was stratified throughout summer and early fall (Fig. 6). During this time the thermocline deepened slightly from 5 m on 29 June to 8 m on 30 September. Between 30 September and 27 October the epilimnion cooled substantially and deepened to ~ 11 m as the metalimnion

eroded. Within the next 2 weeks the pond became nearly isothermal, although very slight chemical stratification persisted until at least 15 November. By 16 January the pond was chemically homogeneous. Because atmospheric deposition and ground-water exchange data are lacking, a whole-lake chemical budget following turnover is unavailable. We can, however, calculate rates of change in water chemistry of the hypolimnion during stratification.

Fluxes determined from hypolimnetic monitoring are subject to error due to, among other things, vertical diffusion of ions across the thermocline. In general, water-column stability is the dominant factor controlling the rate of mass transport. Brunt-Väisälä frequencies (N^2 , s^{-2}) were calculated to determine water-column stability over each 1-m depth interval. Changes in ion concentrations below 11-m depth were used to determine hypolimnetic flux rates. At 11-m depth N^2 ranged from 6.1 to $9.7 \times 10^{-4} s^{-2}$ measured on 29 June and on 6, 15, and 30 September. These frequencies were related to eddy diffusion coefficients (K_z , cm^2

Table 4. Alkalinity balance of the hypolimnion of Mares Pond at depths >11 m for three time intervals during summer stratification. Individual ion fluxes represent the amount of Alk produced (+) or consumed (-) in $\text{meq m}^{-2} \text{d}^{-1}$. Alk_{calc} is the sum of Alk produced by reactions of individual ions. Values in parentheses are percent contribution to Alk_{calc} ; 8% of lake volume and 23% of sediment area lie below 11-m depth.

Ion	29 Jun-6 Sep	6-30 Sep	29 Jun-30 Sep
Alk	1.07	2.28	1.38
Alk_{calc}	1.12	2.88	1.57
SO_4^{2-}	0.32(29%)	1.37(48%)	0.59(38%)
Fe^{2+}	0.48(43%)	0.94(33%)	0.60(38%)
NH_4^+	0.13(12%)	0.40(14%)	0.20(13%)
NO_3^-	0.03	0.005	0.02
Ca^{2+}	0.01	0.14	0.04
Mg^{2+}	0.04	0.002	0.03
Na^+	0.07	0.05	0.07
K^+	0.02	-0.02	0.01
Mn^{2+}	0.02	0.003	0.01

s^{-1}) for mass with empirical data for lakes of morphometry similar to Mares Pond (ELA Lakes 227 and 224; Quay et al. 1980). The model used was $\log_{10} K_z = -5.34 - 0.747 \times (\log_{10} N^2)$, $N = 4$, $r^2 = 0.64$, $\text{SE}_{\text{intercept}} = 1.30$, $\text{SE}_{\text{slope}} = 0.393$, $\text{RMSE of model} = 0.77$. On the basis of this model the calculated values of K_z at 11 m were $0.82-1.2 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. The estimated flux of chemical species across 11-m depth was always <3% of observed changes in the mass of ions in the hypolimnion during stratification.

Ion flux calculations were made for the hypolimnion during the interval of stratification from 29 June to 6 September and during the interval from 6 to 30 September (Table 4). SO_4^{2-} and NO_3^- were the only ions depleted in both intervals, while Alk, NH_4^+ , SRP, and Fe^{2+} increased (Fig. 7). For the most part ion fluxes were higher during the second interval (Table 4). For example, consumption of SO_4^{2-} increased from $0.16 \text{ mmol m}^{-2} \text{ d}^{-1}$ during July and August to 0.68 during the 24-d interval in September. The variation in flux rates may be due to decreasing hypolimnetic oxygen content over summer; as the electron acceptor O_2 is depleted, the use of SO_4^{2-} increases (Fig. 7).

As with the microcosms, major cation concentrations varied little during stratification. The lack of significant sediment cation flux is similar to that found by Carignan

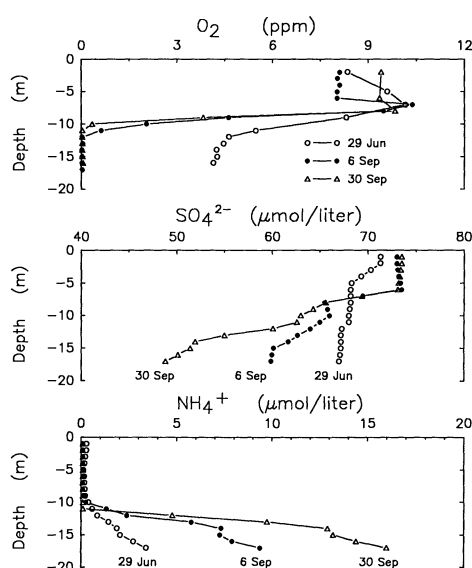


Fig. 7. Oxygen, SO_4^{2-} , and NH_4^+ concentrations vs. depth in Mares Pond during stratification, 1988.

(1985) and Baker et al. (1988). In contrast, various studies of ELA lakes have shown significant releases of cations from sediments in exchange for H^+ (Schindler et al. 1986; Cook et al. 1986; Schiff and Anderson 1987). The magnitude of cation exchange varies annually and may be related to the oxygenation history of the lake (Cook et al. 1986). Part of the reason for low cation fluxes found in the present study may be the relatively high pond-water pH (6.6-7.3) compared to the pH of ELA lakes ($\sim 5-7$) and to different cation exchange capacities of the sediments. Cation concentrations are considerably lower in waters of the ELA lakes compared to these coastal ponds, thus increasing the exchange potentials at given H^+ concentrations.

Comparisons to microcosms—Ion fluxes in the hypolimnion of Mares Pond during September were very similar to fluxes determined in the anoxic microcosms (Table 2). The most comparable microcosm rates are those taken from the first 19 d following experimental turnover and correspond to a similar observation period in the pond (6-30 September). After day 22, SO_4^{2-} disappeared and FeS precipitated from overlying water in the anoxic microcosms, and the fluxes of all ions except NH_4^+ decreased. Fluxes taken over the entire microcosm in-

Table 5. Alkalinity balance for overlying water in sediment microcosms from Mares and Gull Ponds. For Mares, all values are means of three cores ± 1 SE of ion changes in meq m^{-2} from day 3 until the end of the experiment. Balances for Gull cores G1 and G2 are calculated from day 7 until the end of the experiment. Alk_{calc} is the mean value of individual core balances calculated by summing contributions of all ions shown. Percent calculations are based on the value for Alk_{calc} .

	$\text{Alk} = \text{Alk}_{\text{calc}}$	SO_4^{2-}	NO_3^-	NH_4^+	Fe^{2+}
Mares					
Anoxic	$67 \pm 13 = 67 \pm 12$ % of $\Sigma = 67$	28 ± 4 42	0.01 ± 0.4 <1	19 ± 6 28	20 ± 0.5 30
Turnover	$-39 \pm 2 = -36 \pm 5$ % of $\Sigma = 36$	-14 ± 2.0 39	-7.7 ± 0.8 21	-6.0 ± 0.2 17	-8.2 ± 1.6 23
Gull					
G1	$-56 = -58$	-6.1	-31	-22	—
G2	$15 = 22$	-0.1	-3.0	25	—

cubation are thus less comparable to in-lake fluxes; in the hypolimnion of Mares Pond, where the volume of water above sediments was greater than the corresponding volume in the microcosms, SO_4^{2-} concentrations remained above $45 \mu\text{M}$ and FeS was strongly undersaturated.

The substantially lower net rate of SRP release from in-lake sediments compared to the rate observed in the microcosms may be due in part to nutrient uptake by organisms in the hypolimnion. The light attenuation coefficient on 6 September was 0.35 ± 0.01 (SE) m^{-1} and the 1% light level was at 13.1 m. This illumination would allow some autotrophic growth in water and surficial sediments of the upper hypolimnion. The rates of consumption and release of SRP as well as Fe^{2+} are generally similar to fluxes determined in other oligomesotrophic lakes (Kelly et al. 1982) but are lower than fluxes found in eutrophic systems (Kamp-Neilsen 1974).

The excellent correspondence in fluxes determined from microcosms taken at a single site and from the entire hypolimnion in Mares Pond may be atypical. For example, in other systems rates of sediment metabolism (Jones and Simon 1981) and storage of reduced S compounds (White et al. 1989; Giblin et al. 1990) are known to increase with increasing lake depth.

Alkalinity budgets—The importance of various redox and ion exchange reactions to Alk flux was estimated by constructing Alk balances. For Mares Pond, anoxic cores released a total of 67 ± 13 (SE) meq m^{-2} Alk

during the 40-d experiment (Table 5). Reactions involving SO_4^{2-} , NH_4^+ , NO_3^- , and Fe^{2+} generated a calculated sum of 67 ± 12 (SE) meq m^{-2} Alk in the same cores. SO_4^{2-} reduction accounted for most of this Alk increase (42%), while reactions involving Fe^{2+} and N contributed 30 and 28%. Reactions with S were most important to Alk balance during September as well (48%; Table 4). Contributions to Alk from Fe^{2+} reduction were similar between pond and microcosms.

In the Mares Pond turnover cores, measured Alk flux and Alk flux calculated from the sum of redox and exchange reactions were also very similar [-39 ± 2 and -36 ± 5 (SE) meq m^{-2} , respectively]. Oxidation of reduced S dominated Alk consumption (39%). Fe oxidation and nitrification were of similar importance (Table 5).

In contrast to Mares Pond, reactions with N dominated the Alk balances in Gull Pond cores. Nitrification was responsible for 91% of the Alk consumption in core G1; in core G2, NH_4^+ production was responsible for all of the Alk generated from day 7 until the end of the experiment (Table 5).

The magnitude of denitrification in Mares Pond, and its importance to the Alk budget, may be small relative to other reactions with N and S. Given the good Alk balances, NO_3^- reduction can be estimated from the whole-lake inventory of NO_3^- measured in January 1989 (13.9 meq m^{-2}) compared to the inventory during stratification (0.7 meq m^{-2} , September 1988). On this basis, and assuming that NO_3^- reduction is the only process

removing NO_3^- from the lake, 13.2 meq m^{-2} Alk would be produced annually. Although this estimate is a lower bound because sources of NO_3^- have not been included, it is $<10\%$ of the 146 meq m^{-2} Alk produced in the hypolimnion from 29 June to 30 September 1988 (Table 4). Although Alk consumption during oxic phases will decrease net Alk generation, it appears that NO_3^- reduction may be less important than SO_4^{2-} reduction to Alk generation in this pond. This finding compares to the finding of Rudd et al. (1986a) who showed denitrification to be perhaps 4–5 times more important than SO_4^{2-} reduction to Alk generation in some north temperate lakes.

Discussion

Rates of Alk production measured in the water and in the anoxic cores of Mares Pond (1.07 – 2.28 and $2.66 \text{ meq m}^{-2} \text{ d}^{-1}$, respectively) were similar to values reported for other lakes. Carignan (1985), on the basis of pore-water profiles, reported a mean Alk flux of $0.57 \text{ meq m}^{-2} \text{ d}^{-1}$ from the sediments in Clearwater Lake, Ontario. In a similar study with pore-water profiles, Schiff and Anderson (1986) compared several lakes and reported Alk production ranging from 0.06 to $1.4 \text{ meq m}^{-2} \text{ d}^{-1}$ in epilimnetic sediments. Alk production in limnocorrals placed in two ELA lakes and then acidified ranged from 0.65 to $5.7 \text{ meq m}^{-2} \text{ d}^{-1}$ (Schiff and Anderson 1987). The highest rates in that study may be due to stimulation of NO_3^- and SO_4^{2-} reduction by addition of HNO_3 and H_2SO_4 . Net rates based on annual whole-lake budgets range from 0.32 (Schindler et al. 1986) to 0.82 – $1.0 \text{ meq m}^{-2} \text{ d}^{-1}$ (Cook et al. 1986).

Alk consumption in Mares Pond cores that were oxidized to simulate turnover was rapid initially ($3.5 \text{ meq m}^{-2} \text{ d}^{-1}$) and declined over time. Maximal Alk consumption in Gull Pond cores was similar ($4.2 \text{ meq m}^{-2} \text{ d}^{-1}$). Not only are these consumption rates up to twice the Alk production rates, but in Mares Pond half of all Alk lost during the 40-d experiment was consumed in the first 4 d after turnover began. Although much of the Alk consumption resulting from turnover occurs rapidly, the ratio of time-of-anoxic to time-of-oxic conditions in the wa-

ter column may be important in determining annual Alk flux.

Anoxic hypolimnetic sediments often produce Alk at a greater rate than do sediments oxidized at the surface—but not always. For example, the net Alk production for some periods in the oxidized Gull Pond cores equaled the long-term production in anoxic mud from Mares Pond. Hypolimnetic sediments may vary in their response to turnover, as seen in the Gull Pond cores. In these cores, a brief period of Alk consumption after turnover was followed by Alk production due to SO_4^{2-} reduction and NH_4^+ release. After about 20 d, SO_4^{2-} reduction ceased or was reduced to a point where sulfide oxidation in surface layers dominated, and SO_4^{2-} was again released to the overlying water. We have laboratory and field data (unpubl.) suggesting that in some lakes organic C may limit SO_4^{2-} reduction, thus reducing the potential for Alk production. The magnitude and duration of these periods of Alk production may depend therefore on the inventory and quality of C available at depth, in addition to the supply of substrate and extent of oxygen penetration. If the resumption of net Alk generation following sediment oxygenation is common in lakes, it may reduce or at least delay the effects of reoxidation after turnover.

Seasonal turnover can affect epilimnetic and metalimnetic sediments as well, although changes in sediment redox conditions may be less dramatic. In epilimnetic sediments, and in hypolimnetic sediments exposed to oxygen, net Alk flux is a balance between reduction reactions in deeper layers of anoxic sediment and oxidation reactions at the surface. Rudd et al. (1986a) found that 27–35% of the Alk generated in epilimnetic sediments in summer was consumed by sulfide oxidation in fall and winter in ELA Lake 302. Any effect of oxidation on epilimnetic Alk flux may be magnified by changing temperature. For example, published Q_{10} values for SO_4^{2-} reduction are ~ 3 and those of NO_3^- reduction are ~ 2 (Fenchel and Blackburn 1979). The sensitivity of these reactions to temperature could explain an observed net loss of Alk in winter. The argument assumes that reactions generating H^+ , such as Fe^{2+} oxidation, can

proceed abiotically or are less sensitive to temperature change than SO_4^{2-} or NO_3^- reduction. If SO_4^{2-} reduction is less intense after fall turnover, the Alk balance shifts toward consumption. Although epilimnetic sediments can contribute the majority of alkalinity produced in a lake (Kelly and Rudd 1984), the specific roles and interactions of sediment oxygenation and temperature on Alk flux following turnover are unresolved.

The effect of turnover on the whole lake also depends on the relative distribution of hypolimnetic and epilimnetic sediments (cf. Kelly *et al.* 1982). For example, only 8% of the volume of Mares Pond is contained in the hypolimnion, and thus the Alk generated there during summer stratification is much diluted as the pond is mixed during turnover. In lakes with larger hypolimnia, such as ELA Lake 227 where hypolimnetic volume is about 36% of total volume, the effect of fall turnover on lake chemistry is more pronounced (Cook 1981).

The relative importance of redox reactions to sediment-water Alk flux varies among lakes for reasons not entirely understood, but related to oxygenation, substrate availability, and total sediment metabolism. In Mares Pond cores, water-column aeration resulted in a dramatic shift from net SO_4^{2-} reduction to sulfide oxidation. Such shifts following aeration are not universal, however, because net SO_4^{2-} reduction often occurs in epilimnetic sediments (Kelly and Rudd 1984). In aerated Gull Pond cores both net SO_4^{2-} reduction and sulfide oxidation occurred. This disparity highlights the dynamic nature of S reactions in sediments and indicates that the oxygen content of overlying water alone fails to predict whether a sediment will store or lose S. The availability of S and N as electron acceptors or donors affects relative magnitudes and rates of reaction in some lakes (Andersen 1977; Cook and Schindler 1983; Mitchell *et al.* 1988), but not in others (Rudd *et al.* 1986a). In our study ponds there was no evidence for concentration dependence of rates with either N or S. For example, rates of SO_4^{2-} reduction in Mares Pond cores remained constant even as SO_4^{2-} concentrations approached zero (Fig. 2). Be-

cause SO_4^{2-} concentrations in Mares and Gull Ponds were very similar, their effects also cannot explain why S reactions were more important to Alk flux in Mares Pond than in Gull Pond. One possible explanation for the greater importance of S reactions in Mares Pond than in Gull may be related to organic matter loading and hypolimnetic respiration in these ponds. Rich (1980) determined that production and overall hypolimnetic metabolism was higher in Mares Pond than in Gull. It is unclear at present whether the importance of reactions using various electron acceptors to Alk budgets can be correlated with productivity or whole-lake metabolism across a variety of systems. Finally, the relative importance of reactions such as SO_4^{2-} reduction may be limited by low organic C concentrations in some environments, especially when reactions occur at depth, as in epilimnetic sediments.

S dynamics play a substantial role in the Alk budgets of many lakes. In our experiments the reoxidation of S occurred rapidly in response to turnover, and, although H_2S may have been oxidized initially, the oxidation of solid-phase species probably dominated after 1 or 2 d. This finding contrasts with the study of ELA Lake 227 by Cook (1981), who found little oxidation of sediment FeS during turnover. Cook did report complete oxidation of H_2S stored in the water column after turnover. Our results demonstrate the potential for reoxidation of reduced S stored in sediments as well.

There is little known about the oxidation rates of different S species from natural sediments. In the laboratory, biological plus chemical oxidation rates of FeS_2 can reach $7.8 \text{ mmol S (g FeS}_2\text{)}^{-1} \text{ d}^{-1}$, although typically rates range from 0.07 to 1.0 (Taylor *et al.* 1984; Moses *et al.* 1987). Calculated oxidation rates of FeS_2 in Mares Pond sediments were $0.17\text{--}0.21 \text{ mmol S (g FeS}_2\text{)}^{-1} \text{ d}^{-1}$ and are within the range of measured laboratory rates (Taylor *et al.* 1984; Moses *et al.* 1987). These oxidation rate calculations assume that SO_4^{2-} appearing in overlying waters after turnover originated from the upper 3 cm of sediment and that 80% of the CRS fraction was FeS_2 (80% value measured by Giblin *et al.* 1990). The calculated

oxidation rates per unit of weight of FeS_2 will be upper bounds if oxidation of organic S contributes to SO_4^{2-} appearance in overlying waters. In general, the oxidation potential of acid-volatile S (AVS; Fe monosulfides and $\Sigma\text{H}_2\text{S}$) is slightly greater than that of FeS_2 (Moses et al. 1987). Wieder and Lang (1988) reported that FeS oxidized faster than FeS_2 during incubations of peat from a bog in Virginia.

Organic S may be the form of S least susceptible to oxidation. For example, Rudd et al. (1986a) found preferential oxidation of inorganic vs. organic S in sediments of ELA Lake 302 and argued that this loss explained the increasing fraction of organic S with depth in sediments of several other lakes. Both organic and inorganic fractions can be oxidized; the percentage of each fraction oxidized in any sediment may vary and within-lake variability can be substantial. In Mares Pond the isotopic balances indicate that both fractions were oxidized, in agreement with Rudd et al. (1986a). The reasons for the wide range of percent CRS oxidized in this study (30–70%) and the ELA study (31–83%) are unclear. In our sediments S_T and S_{org} change rapidly with depth, which places limits on the resolution of isotopic mass balances. Further studies must thus address the controls of organic vs. inorganic S formation and oxidation in different lakes in order to understand the role of sulfide storage and oxidation in Alk dynamics.

Oxidation effects following seasonal turnover should be considered in studies that address the history of increasing acid precipitation by dating sediments where increases in S are found (Holdren et al. 1984). The accuracy of such measurements has been questioned (Rudd et al. 1986b) because SO_4^{2-} and H_2S may diffuse several centimeters in sediments before they are reduced or precipitated. In addition, our results indicate that seasonal patterns of reduced S accumulation followed by loss from oxidation during turnover will affect these paleolimnological estimates. For example, the sedimentation rate since 1900 in Mares Pond at 11-m depth is about 0.83 mm yr^{-1} (Giblin et al. 1990). If the inventory of S available for reoxidation is limited to 3- or

4-cm depth during turnover, then the corresponding error on any S-based stratigraphic age estimate from this lake could be $\pm 35\text{--}50 \text{ yr}$. Such smearing of sedimentary records must be considered when studying hypolimnetic, and perhaps epilimnetic, sediments from lakes that turn over regularly and especially from lakes that turn over rarely.

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